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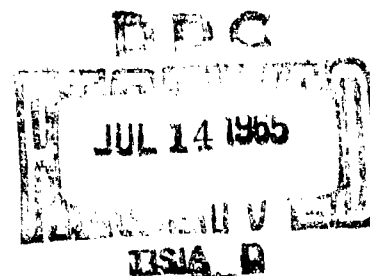
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HEAT RESISTANT EXPLOSIVES XIX.
AN IMPROVED SYNTHESIS OF
2,2',2'',4,4',4'',6,6',6''-
NONANITROTERPHENYL, NONA (C)

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HEAT RESISTANT EXPLOSIVES XIX.
AN IMPROVED SYNTHESIS OF
2,2',2'',4,4',4'',6,6',6''-NONANITROTERPHENYL, NONA (C)

by

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ABSTRACT: Improved procedures for the preparation of 2,2',2'',4,4',4'',6,6',6''-nonanitroterphenyl, NONA, from picryl chloride and 1,3-dichloro-2,4,6-trinitrobenzene or 1,3-dibromo-2,4,6-trinitrobenzene have been developed. The NONA is formed in yields of approximately 25% along with quantities of 2,2',4,4',6,6'-hexanitrobiphenyl, HNB, and small amounts of other products. By the use of thin-layer chromatography and a novel fractional crystallization from acetone, the separation of products has been greatly simplified. An improved procedure for the recrystallization of the crude product from acetone produces relatively large prisms whose bulk density is approximately 0.70.

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This report describes improved procedures for the synthesis of 2,2',2'',4,4',4'',6,6',6''-nonanitroterphenyl, NONA, a thermally stable high explosive suitable for use at very high temperatures in mild detonating fuses, MDF, flexible linear shaped charges, FLSC, and other explosive components for special applications in high speed aircraft, space craft, etc. This compound has been described in NavOrd Report (NOL) 6904 which is part VIII in the series Heat Resistant Explosives. This work was carried out in part under the Foundational Research Fund, Task FR-44, and in part under the Study of Explosive Properties, Task RUME-4E-000/212-1/F008-08-11, Problem 012.

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By direction

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INTRODUCTION

As a result of a study of the thermal decomposition of TNT (1), it was predicted that the compound 2,2',2'',4,4',4'',6,6',6''-nonanitroterphenyl, NONA, would have unusual high temperature stability. A report of the synthesis of this compound was made soon thereafter (2) and preliminary examination showed that this prediction was correct. A more thorough study later showed this explosive to be well suited for use in mild detonating fuses, MDF, and flexible linear shaped charges, FLSC, and that it was capable of functioning after exposure to temperatures above 400°C (3). The original preparation involved a mixed Ullmann reaction with picryl chloride, Picl , and 1,3-dichloro-2,4,6-trinitrobenzene, DiClTNB . The compound 2,2',4,4',6,6'-hexanitrobiphenyl, HNB, rather than NONA, was the primary product. The NONA was isolated by a combination of extraction and chromatographic procedures. Although the mixed Ullmann reaction appeared to be the only reasonable route to this compound, the method did not lend itself to large scale preparation.

The successes of 2,2',4,4',6,6'-hexanitrostilbene, HNS, (4,5) and dipicramide, DIPAM, (6,7), as heat resistant special applications explosives were outstanding. However, the applications of these compounds are limited by their melting points, 316°C and 305°C, respectively. It was anticipated that needs would arise for high explosives capable of functioning at still higher temperatures; consequently, the interest in NONA, which melts in the range 440-450°C, was increased and a search for an adequate method of preparation was accelerated. The effort in that direction is summarized in this report. The method of preparation still involves the relatively low yield mixed Ullmann reaction, but improvements have been effected and the isolation has been simplified. The major product from the preparation is still HNB; however, efforts are being made to find a use for this compound in our explosives program.

RESULTS AND DISCUSSION

Early work on the synthesis on NONA clearly indicated that there were two areas in which improvements were needed before any large scale preparation was undertaken. First, it was desirable to find a new route to the compound or to improve the yields in the existing synthesis. Secondly, if the mixed Ullmann reaction was to be used, there was a critical need for improved procedures for the isolation and identification of the reaction products. After a search of the literature, it was concluded that the mixed Ullmann reaction was probably the most promising route to follow.

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In the Ullmann synthesis of unsymmetrical biaryls, Forrest (8,9) has found that best results are obtained when one reactant is activated by electron attracting groups at the ortho positions and the other is unactivated or activated to a lesser extent. The less active compound should be present in excess. He also found that in going from iodo derivatives to chloro derivatives the iodo compounds were the most active, the chloro compounds the least active and the bromo compounds were intermediate. Since it was necessary that the reactants be fully nitrated prior to the condensation*, it was not possible for us to use starting materials that differed in the degree of activation due to substituents. However, in efforts to find conditions which favored the formation of NONA over HNB, considerable work was done using mixed halides. With iodides, we were generally unsuccessful which was probably due to side reactions of the iodine. Moreover, the cost and availability of these compounds made them undesirable starting materials. Mixtures of bromides and chlorides gave about the same results as when PiCl was condensed with DiClTNB , but the reactions could be run at somewhat lower temperatures. It was with DiBrTNB and an excess of PiCl that our first large scale preparation of NONA was made.

In efforts to find an adequate procedure for the separation of NONA from the other reaction products, a search for suitable methods of crystallizing the compound was initiated. Crystallization from numerous pure solvents by conventional procedures was tried and found totally unsuccessful. Although the solubility of NONA in most solvents is low, it is appreciably soluble in acetone, tetrahydrofuran, epichlorohydrin and methyl ethyl ketone. However, when hot saturated solutions in these solvents were cooled in the refrigerator no appreciable crystallization occurred. It thus appeared that the variation of solubility with temperature, at least in these solvents, was very slight. The use of mixed solvents such as acetone-methanol and acetone-hexane produced crystals of very fine particle size that readily acquired static charges. Such solvent systems were not effective in separating NONA from HNB and other reaction products. It was subsequently found that solutions in pure solvents such as those listed above gave beautifully crystalline NONA when concentrated by distillation. It was also found that by using this technique with acetone solutions, reasonably good separations of NONA from HNB could be effected.

* We know of no instance where unnitrated or partially nitrated polyphenyls have been nitrated to the trinitrophenyl stage without the activating effect of electron releasing substituents. Our efforts to achieve this were not successful.

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Using PiCl , DiBrTNB and electrolytic copper dust in nitrobenzene, a 0.5 molar (DiBrTNB) run was made. A solution of 1.25 moles of PiCl in dry nitrobenzene was heated to $115-118^\circ\text{C}$ and a dry mixture of the DiBrTNB and 2.25 moles of copper was added portionwise over a period of approximately one hour. An additional 0.63 moles of copper was then added over a ten minute period after which the reaction mixture was filtered while hot. The solvent was removed by steam distillation and the dark residue was digested in boiling methanol and recovered by filtration. It was then dissolved in acetone, treated with charcoal, concentrated to a volume of about 500 ml and filtered while hot. The yield was 66 g (21%) of a crystalline product which showed no tendency to melt at 300°C , and gave an excellent X-ray diffraction pattern for NONA. A sample of this material gave 1.86 cc of gas/g/hr in a two hour vacuum stability test at 260°C . Although this is not as good as would be expected of purified NONA it is excellent for a crude product. An additional 3 g of solids which did not melt at 300°C were recovered by adding ethanol to the filtrate and concentrating further. The X-ray diffraction pattern of this product indicated that it was not NONA. On recrystallizing the combined crude products from acetone an 87% recovery of beautifully crystalline NONA was made. An additional 5% was recovered by adding glacial acetic acid and concentrating further.

Using essentially the above procedure at reaction temperatures of approximately 125°C , 10.7 moles of DiBrTNB were converted to 1.57 moles (1008 g; 15% yield) of purified NONA in fifteen runs. The lower overall yield was probably due to our failure to consistently duplicate the conditions of the 0.5 molar run above. The main difficulty probably lay in the isolation of products from the various runs. This has been substantiated by later findings in the isolation procedure. Attempts were made to obtain second crops of the crude product by cooling the filtrate, filtering off the solid which formed, adding glacial acetic acid, concentrating until precipitation occurred and filtering while hot. Approximately 200 g of a finely divided solid which did not melt at 300°C was recovered in this manner. It gave more than 5 cc of gas/g/hr in the vacuum stability test at 260°C and X-ray diffraction indicated that it was primarily NONA contaminated with other products. Its solubility characteristics indicated that the contaminants were probably higher molecular weight materials. Attempts to purify this material by recrystallization were not successful.

In efforts to find suitable methods of monitoring the various fractions for content, visible, ultraviolet and infrared spectra were tried. As was expected, the spectra of the

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primary products were too similar to be of value. Although X-ray diffraction gave distinct and different patterns for the known members of the polymer-homologous series 1,3,5-trinitrobenzene (TNB), HNB, NONA, 2,2',2'',2''',4,4',4'',4''',6,6',6'',6'''-dodecanitroquarterphenyl (DODECA)*, etc., it was not sensitive enough to detect the presence of small quantities of one in the presence of larger quantities of another. The application of thin-layer chromatography (TLC) to this problem proved quite successful. By chromatography on thin layers of silica gel using benzene as a developer, mixtures of HNB and NONA were separated into two distinct zones. The zones were visualized by spraying with saturated methanolic solutions of sodium or potassium hydroxide. The distance which each of the compounds traveled, i.e., the R_f values, differed from chromatogram to chromatogram and was probably a function of the water content of the adsorbent. The R_f values for HNB ranged from 0.37 to 0.50 and those for NONA from 0.29 to 0.39. However, in a large number of chromatograms, the R_x values** for NONA, using HNB as the standard, were 0.76 - 0.78. By using this technique we were able to separate the crude reaction mixture, including unreacted starting materials, when present, into its various components. The R_x value for DODECA was 0.69 and those for $PICl$ and $DiClTNB$ were 122 and 150, respectively. Under the conditions used, TLC failed to separate TNB from HNB. Although TNB has been found among the reaction products, it is removed during the methanol digestion and therefore poses no problem in the isolation of NONA in either of the two procedures given in the experimental part of this report.

Using TLC in conjunction with crystallization from acetone, it was found that the first crop of crystals precipitated was usually a good grade of NONA containing a small amount of HNB. The precipitate which formed on cooling the filtrate was almost pure HNB. The process was repeated to give three crops of NONA and two crops of HNB. The residue from the third crop of NONA was shown by TLC to contain appreciable HNB, some NONA and a considerable quantity of DODECA along with smaller amounts of what appear chromatographically to be higher members of the series.

* This compound has been prepared in this laboratory and will be the subject of a future report.

** The R_x value is defined as the distance a substance travels on a chromatogram divided by the distance traveled by a standard on the same chromatogram(10).

Having developed a workable method for the isolation of NONA from the reaction mixture and an excellent qualitative analytical procedure, it was desired to determine the effects of reaction temperature on the yields of NONA. A series of reactions were run using both DiBrTNB and DiClTNB at temperatures ranging from 100°C to 150°C. The conditions and results of this series of reactions are given in Table 1. In these reactions, solutions containing both organic reactants were added to stirred refluxing slurries of copper bronze. Except in runs 10 and 11, 50% excesses of PiCl were used. In run 10 PiCl was used in 100% excess, whereas the theoretical amount was used in run 11. These runs were made to determine the effects of varying the amount of PiCl used on the yields of NONA. When runs 10 and 11 are compared with run 5, which was carried out at approximately the same temperature, the effect of using the theoretical amount, a 50% excess, and a 100% excess of PiCl is observed. The solvents were toluene and mixtures of nitrobenzene-benzene and nitrobenzene-toluene which gave the desired pot temperatures at reflux. The total reaction time for each reaction was approximately twenty minutes, and the ratio of solvent (vol) to reactants (wt) was kept approximately constant throughout the series. The compositions listed for the solvents in the table are approximations. Solvents having the desired boiling points were prepared by starting with the listed compositions and adding to or distilling from the mixtures small volumes of the more volatile components.

With DiBrTNB and an excess of PiCl the only decidedly lower yields were in runs 3 and 4 at 110°C. However, no conclusive explanation can be given for the larger yield in run 1 at 100°C. The lower yield in run 3 may be due in part to the fact that the quantities of materials used were smaller. It has been found that the method of isolation tends to give better results in larger runs. In several small exploratory runs, which are not listed in the table, the yields were consistently lower than those in larger runs at the same temperatures. The yields were consistently above 20% at temperatures of 123°C to 135°C, the best being at 123°C. The lowest yield was in run 9 in which the reaction temperature was 148-150°C. The acetone solution of the crude product from this run was much darker than usual probably due to a greater "tar" formation. In run 10 where a 100% excess of PiCl was used, the yield is slightly less than that in run 5 which was carried out at approximately the same temperature with a 50% excess of PiCl . As shown in run 11, the reduction of the amount of the PiCl used to the theoretical amount results in an appreciable reduction in the yield of NONA. The reactants in runs 12 through 15 were PiCl and DiClTNB. The low yield in run 12 may be due both

TABLE 1
The Preparation of NONA

Run	Reactants		Moles		Solvent/a	Temp. °C	% Yield	
	Ar	Ar'	Ar	Ar'			NONA/b	HNB/c
1	PICl	DiBrTNB	0.375	0.127	NB-Benz 1:1	100	21.5	47.6
2	"	"	0.375	0.127	Tol	112	20.3	50.0
3	"	"	0.30	0.10	NB-Benz 3:2	110	15.8	52.8
4	"	"	0.37	0.124	"	110	17.8	53.0
5	"	"	0.375	0.127	"	123-124	25.8	42.8
6	"	"	0.39	0.13	NB-Tol 1:1	133	23.0	32.4
7	"	"	0.375	0.127	"	135	21.7/d	--
8	"	"	0.375	0.127	"	135	21.7/d	--
9	"	"	0.375	0.127	"	148-150	12.0	33.3
10	"	"	0.52	0.13	NB-Benz 5:2	121-124	22.7	66.8
11	"	"	0.26	0.127	"	123-125	17.4	41.0
12	"	DiClTNB	0.20	0.065	Tol	112	16.0	42.7
13	"	"	0.39	0.13	NB-Tol 2:9	123	20.6	50.6
14	"	"	0.39	0.13	"	134	25.2	31.5
15	"	"	0.39	0.13	"	146	21.1	49.5

/a Legend: Benz = benzene; Tol = toluene; NB = nitrobenzene.

/b Yield of recrystallized product.

/c Yield of crude product. /d Crude products combined and recrystallized together.

to the small size of the run and the low reaction temperature. The best yield in this group was at 134°C and there was little difference between the runs at 123°C and 146°C. In each of the runs using DiBrTNB, the reaction was sufficiently exothermic that once it was started the external heating could be removed and the rate of reflux controlled by the rate of addition. This was not the case when DiClTNB was one of the reactants, the heating could be reduced but not removed entirely.

The yields of HNB given in the last column of the table are yields of crude product and are based on the total PiCl used. This material can be recrystallized from toluene or acetone-hexane with about a 90% recovery. In this work no special attention was given to the isolation of this product and mechanical losses are to a large extent responsible for the variations in yields. Should a use be found for HNB, it could probably be isolated in somewhat greater yields than those given.

The results of this work indicate that NONA can be made equally well with either DiBrTNB or DiClTNB in reactions with PiCl . In large scale preparations, the choice would probably be made on the basis of cost. It appears that the optimum temperature for DiBrTNB is about 120°C and that for DiClTNB is about 10°C higher. The formation of NONA is probably a stepwise process involving several reactions rather than the simultaneous combination of two mole of PiCl with one of the dihalide. The formation of HNB from two moles of PiCl is a competing reaction. Efforts to find methods of combining the reactants so as to favor the formation of NONA included numerous exploratory reactions in which the method and sequence of addition were varied. No procedure was discovered which greatly increased the yield of NONA; however, our best results were obtained using the methods described above.

It has been found that toluene, nitrobenzene and the mixed solvents listed in the table can be used with about equal facility. The fact that toluene gives slightly lower yields may be due to its lower boiling temperature. The American Cyanamid Company (15) has found that the reaction goes well in Xylene and that by using this solvent, the steam distillation step can be eliminated. We have found that when toluene is used a major portion of the products, including most of the NONA, is precipitated and remains with the inorganic residue on filtration. The organic material is recovered by washing the filter cake with acetone and the solution may be worked up separately or combined with the toluene filtrate. If the reaction mixture is kept hot during the filtration, it is likely that a preponderance of the HNB would be found in the toluene filtrate.

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Since steam distillation not only removes the reaction solvent, but removes any water soluble impurities it was retained as part of the isolation procedure in this study. When it is followed by methanol digestion, the product is essentially a mixture of HNB, NONA, DODECA and apparently higher members of the series. Along with these, however, are some highly colored products ("tars") most of which can be removed by carbon treatment.

In the previously mentioned 0.5 mole run in which a dry mixture of DiBrTNB and copper dust was added to a solution of PiCl in nitrobenzene at $115-118^\circ\text{C}$, the yield of recrystallized NONA was 19.3% even though the method of isolation was not thoroughly worked out at the time. With the improved isolation procedure, it is likely that this method would produce yields that compare favorably with those in the table. However, the addition of a liquid to a reaction mixture is more adaptable than the addition of a solid. This mode of combining the reactants coupled with the improved method of isolation is, in our judgment, the preferred procedure for the synthesis of NONA.

In the majority of the runs listed in Table 1, the crude NONA was recovered in three crops. However, mechanical losses are greater when small crops are handled. In view of this fact, when several runs are to be made it is advisable to combine the residues after the second crops of HNB have been removed and recover the remainder of the NONA in larger quantities after several of these residues have been accumulated. In the recrystallization procedure, the first two crops are of an excellent grade but the third crops may contain small amounts of impurities and are frequently of very small crystal size. For this reason, it is advisable to combine the third crops for recrystallization when sizable quantities have been accumulated.

Probably the most critical step in the synthesis is the recovery of crude NONA from the concentrated acetone solutions. It is essential that the solutions be kept warm during filtration to prevent the HNB from precipitating and clogging the funnels. It is also important that the funnels not be hot enough to cause excessive evaporation of the solvent as this will also cause the precipitation of the HNB. Should this difficulty arise, the easiest solution is to redissolve the entire precipitate and start the concentration over again. It is better not to concentrate the initial solution to such an extent as to make it difficult to filter without the precipitation of HNB. This will result in smaller and purer first crops of NONA and the second crops will be larger.

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In a 0.13 mole run in which the Ullmann reaction was carried out at 122-3°C, an attempt was made to eliminate steam distillation as part of the work up. When the reaction was complete, the mixture was filtered as usual and the filter cake was washed with acetone to remove any organic products which had precipitated. The filtrate and washings were then distilled until the temperature of the distillate was 80°C to remove the acetone. A liter of methanol was then added slowly, while stirring and heating, to precipitate the NONA. On filtration, a brown solid was recovered whose damp weight was about 30 g. This was dissolved in acetone, treated with charcoal and the NONA was recovered by concentrating the solution in the usual manner. The yield was 10.9 g (13.2%) in three crops. By adding hexane, cooling and filtering, an additional 2.5 g of solids were recovered from the concentrated mother liquor. Thin layer chromatography indicated that the final product was mainly a mixture of HNB, NONA and DODECA. Although the NONA isolated in this manner was essentially pure, the low yield made this procedure unattractive.

It is essential that starting materials in the coupling reaction be thoroughly dry and free from any impurities containing active hydrogen atoms. Such impurities cause dehalogenation of the aromatic halides and reduce the yields of normal Ullmann products. The PiCl used in this work was Eastman White Label and was used without further purification. The DiBrTNB was prepared by the nitration of *m*-dibromobenzene according to the procedure of Dacons and Taylor (11). The DiClTNB was prepared either by the method of Blais, et al (12), which involves the treatment of the dipyridinium salt of styphnic acid with phosphorous oxychloride, or by a similar procedure using 1,3-dimethoxy-2,4,6-trinitrobenzene (13). Venus Natural Copper, Fine 44-F supplied by U. S. Bronze Powder Works, Flemington, New Jersey, was found to be superior to electrolytic copper dust.

As previously mentioned, numerous procedures for combining the reactants in the NONA synthesis have been explored. The two procedures which were considered best on the basis of ease of application and results have been discussed and are described in detail in the experimental section. The preferred procedure is that which involves the addition of a solution of both organic reactants to a slurry of copper at the desired temperature. The isolation involves steam distillation, methanol digestion and precipitation from acetone solutions. The alternate procedure was developed prior to the use of TLC in this study and consequently prior to the time when precipitation from acetone was thoroughly understood. The yields from the alternate procedure were variable due primarily to the lack of any

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effective method for assaying the products and determining when the bulk of the NONA had been removed from the reaction mixture. This procedure has not been repeated since the more adequate method of isolation has been developed. However, there is reason to believe that the yields from the alternate procedure would compare favorably with those from the preferred procedure if the same method of isolation were used.

EXPERIMENTAL

Synthesis of NONA. A mixture of 300 ml of dry nitrobenzene and 200 ml of dry benzene was distilled until the boiling temperature was 122°C. This mixture was used as the solvent in the following reaction. A slurry of 63 g (1.0 mole) of copper bronze in 125 ml of the reaction solvent was made in a one liter three neck round bottom flask fitted with a mechanical stirrer, addition funnel, condenser, and thermometer. The slurry was heated to reflux with vigorous stirring on a heating mantle held in place by a laboratory jack. A solution of 47 g (0.127 mole) of DiBrTNB and 93 g (0.375 mole) of PbCl_2 in 175 ml of the solvent mixture was added from the addition funnel. Initially 20 ml of this solution was added rapidly and the temperature dropped to 118°C. After two minutes the temperature had risen to 123°C and the copper had lost its metallic sheen. The heating mantle was then lowered and the remainder of the solution was added over a period of five minutes. During this time the temperature was 123-4°C and the reflux was vigorous but not excessive. The heating mantle was again raised into position and the refluxing continued for about five minutes. The mixture was filtered immediately and the inorganic residue was washed first with cold toluene to cool the filter cake and then with acetone until the filtrate was almost colorless. The solvent was removed by steam distillation and the dark residue, after the aqueous layer was decanted, was digested in 700 ml of refluxing methanol with vigorous stirring for a period of fifteen minutes. The suspension was filtered and the light brown residue was thoroughly washed with methanol on the funnel. It was then dissolved in two liters of acetone and treated with 40 g of Darco G-60 and 20 g of Celite at reflux. The mixture was filtered with suction through a glass fiber filter paper and the filtrate was concentrated by distillation. When the volume had been reduced to about 400 ml, crystallization occurred. Concentration was continued until the volume was about 300 ml and bumping made further concentration difficult. The tan solid was recovered by filtration through a jacketed Büchner funnel which had been preheated with steam. Heating of the funnel was discontinued during filtration so as not to cause excessive evaporation of the

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solvent. The product was washed with about 75 ml of acetone-methanol 1:1* and the wash liquor was kept separate. Thin-layer chromatography indicated that the product was NONA contaminated with a small amount of HNB. A small amount of solid which formed in the wash liquor was shown by TLC to contain both NONA and HNB. It was recovered and combined with the crude NONA. After drying on the bench, the first crop weighed 18.1 g. The acetone filtrate was heated to reflux and sufficient acetone was added to dissolve the precipitate that formed during filtration. It was then cooled to 0-5°C and the light tan precipitate was recovered by suction filtration. After air drying, this product weighed 23.2 g and TLC showed it to be nearly pure HNB. The acetone filtrate was returned to the distillation apparatus and concentrated until copious crystallization had occurred and the volume was about 100 ml. A second crop of crude NONA was recovered as described above except that a smaller volume of acetone-methanol was used for washing. This crop weighed 3.6 g and TLC indicated that it was nearly pure. A second crop of HNB was recovered as previously described and on air drying it weighed 11.4 g. By further concentrating the acetone filtrate until the volume was 50-60 ml, a third crop of crude NONA weighing 1.0 g was recovered. The filtrate was shown by TLC to contain mainly HNB, some NONA and an appreciable quantity of DODECA along with traces of other products. This mixture was not resolved. The combined yield of crude NONA was 22.7 g (28.3%). After recrystallization from acetone, the yield was 20.8 g (25.8%).

Alternate Synthesis of NONA. A solution of 310 g (1.25 moles) of PCl_5 in 800 ml of dry nitrobenzene was made in a 2 liter three neck round bottom flask fitted with a mechanical stirrer, powder funnel, and thermometer. The flask was heated by a thermostatically controlled oil bath held in place by a laboratory jack. The temperature of the solution was raised to 110°C and 20 g of a dry mixture of 186 g (0.50 mole) of DiBrTNB and 142 g (2.25 moles) of activated** electrolytic copper dust was added with vigorous stirring through the powder funnel. During the next ten minutes, the temperature was allowed to rise to 115°C and the copper lost its metallic sheen. The remainder of the mixture was added in approximately 10 g portions over a period of one hour. The reaction was exothermic and the oil bath was adjusted so as to reduce the external heating and maintain a reaction temperature of 115-118°C

* One to one mixtures of acetone-ether or acetone-pentane may be used to wash the product and these washes need not be kept separate.

** The electrolytic copper dust was activated by treating with hot concentrated hydrochloric acid, then washed with water, methanol and ether. It was dried under reduced pressure at 100°C for 30 minutes.

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throughout the addition period. When all of the mixture had been added, an additional 40 g (0.64 mole) of copper dust was added over a period of ten minutes. During this period, it was necessary to increase the heating to maintain the temperature of 115-118°C. The reaction mixture was allowed to cool then filtered with suction and the inorganic residue was thoroughly washed with acetone. The acetone and nitrobenzene were removed by steam distillation and, after the aqueous layer was decanted, the dark brown residue was digested for fifteen minutes in one liter of refluxing methanol. The product was recovered by filtration and dissolved in 3.5 liters of acetone, treated with a mixture of 75 g of Darco G-60 and 25 g of Celite at reflux and filtered with suction through a glass fiber filter paper. The filtrate was placed in a 4 liter beaker and evaporated slowly with moderate stirring on a steam bath until the volume was 400-500 ml and copious crystallization had occurred. It was then filtered while hot through a preheated funnel and the product was washed with 400 ml of acetone-ether 1:1 and air dried. The yield was 66 g (21%) of a light yellow, crystalline solid which showed no tendency to melt at 300°C, gave an excellent X-ray diffraction pattern for NONA, and gave 1.86 ml of gas per gram per hour in a two hour vacuum stability test at 260°C. On standing, the filtrate gave 155 g of solid which was not positively identified but the melting range, 220-236°C, indicated that it was impure HNB. On recrystallizing the crude NONA from acetone (see below) the recovery was 92%.

Recrystallization of NONA. A 257 g sample of crude NONA was dissolved in 7.5 liters of acetone and a 3 liter portion of this solution was placed in a 5 liter three neck flask fitted with a mechanical stirrer, addition funnel, and condenser. The flask was heated on a steam bath and the solution was stirred at a moderate rate. When distillation started, the remainder of the solution was added at about the same rate as the distillate was removed. As the concentration progressed, crystallization started. When all of the solution had been added and the volume had been reduced to about one liter, the mixture began to bump and the first crop was removed by suction filtration. The product was washed with methanol and the wash liquor kept separate. A small amount of solid which precipitated in the wash liquor was added to the acetone filtrate. On air drying the first crop weighed 219 g. The acetone filtrate was returned to the distilling apparatus and concentrated to a volume of about 200 ml. The solution was then filtered while hot and the product was washed with methanol as above. On drying, the second crop weighed 16.5 g. The concentration was continued and 150 ml of toluene was added at about the same rate as the distillate was removed. When distillation ceased, the solution was filtered

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while hot and the solid product was washed with toluene. After drying on the bench, the third crop weighed 9.0 g, bringing the total recovery to 244.5 g (95%). Thin-layer chromatography indicated that all three crops were pure NONA. However, crop three was made up of fine crystals and its bulk density was apparently low. Crops one and two were of pale yellow prisms, some as large as 50 x 150 microns. This material poured well and had a bulk density (14) of 0.70.

Thin-Layer Chromatography. The thin-layer chromatographic analyses of the various products and mixtures were carried out qualitatively according to the procedure given by Randerath (10).. Silica gel-G (Research Specialties Co., Richmond, California) or Kiesel gel D-5 (Arthur H. Thomas Co., Philadelphia, Pa.) were used as supports to prepare thin layers 300 microns thick on either 10 x 20 cm or 20 x 20 cm glass plates. The samples were applied to the plates in amounts ranging from 5-10 micrograms per spot from acetone solutions. After air drying, the spotted plates were developed with reagent grade benzene. Visualization of the developed chromatograms was accomplished by lightly spraying the plates with a fine mist of a saturated alcoholic solution of sodium or potassium hydroxide. The zones appeared as bright red spots.

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